

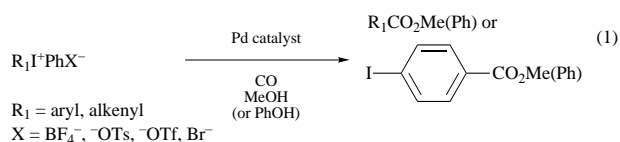
Palladium-catalyzed alkoxy-carbonylation of aryl- and alkenyl-iodonium salts

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The palladium-catalyzed carbonylation of diaryliodonium tetrafluoroborates and tosylates (toluene-*p*-sulfonates) in the presence of methanol and phenol afforded aromatic esters at room temperature under one atmosphere of carbon monoxide. However, carbonylation of diaryliodonium triflates and bromides in methanol afforded 4-iodophenyl-substituted methyl esters.

The carbonylation of aryl and vinyl halides or triflates catalyzed by palladium complexes in the presence of alcohols and phenols represents an important procedure for the synthesis of a variety of aromatic and α,β -unsaturated esters.¹ The carbonylation of aryl bromides and iodides usually can be carried out with Pd(PPh₃)₂Cl₂ as a catalyst under one atmosphere of carbon monoxide in an alcoholic solution, such as *n*-butanol, in the presence of triethylamine, diethylamine, or sodium acetate as base, at 100 °C or less, to provide esters.²⁻⁴ In the case of methyl esters, the reaction is slow at atmospheric pressure at the boiling point of methanol and therefore the reaction requires the use of a higher pressure of carbon monoxide.⁵ In connection with our programs to utilize hypervalent iodine compounds,⁶ we have found that the palladium-catalyzed carbonylation of hypervalent iodonium salts with methanol and phenol as nucleophiles at room temperature and one atmosphere of carbon monoxide affords esters or 4-iodophenyl-substituted esters depending on the counterions present [eqn. (1)].



The results of the palladium-catalyzed carbonylation of hypervalent iodine compounds are summarized in Table 1. Methoxycarbonylation of diphenyliodonium tetrafluoroborate **1a**⁷ was accomplished without using base in the presence of methanol and Pd(OAc)₂ (0.2 mol%) as a catalyst under mild conditions to afford the methyl ester **6a** with high catalytic turnovers under one atmosphere pressure of CO and at room temperature in 93% yield (entry 1, Method A). However, carbonylation of **1a** in the presence of phenol was carried out in the presence of 1 equiv. of NaOH and PhOH in DMF to provide the phenyl ester **7a** (entry 1, Method B). In this reaction, the presence of NaOH (1 equiv.) was crucial. For the *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate **2a**,⁸ during carbonylation in the presence of methanol and phenol, the *p*-methoxyphenyl group was transferred and *p*-methoxybenzoic acid esters **6b** and **7b** were obtained as the sole products (entry 2, Method A and B). By utilizing 2-thienyl(phenyl)iodonium tosylate **3a**,⁹ 2-thienylcarboxylic acid ester **6c** and **7c** were successfully afforded (entry 3). This methodology was also applied to alkenyliodonium tetrafluoroborate **4**⁷ to provide α,β -unsaturated ester **7d**. Accordingly the iodonium salt **4** was

Table 1 Palladium-catalyzed alkoxy-carbonylation of hypervalent iodine compounds

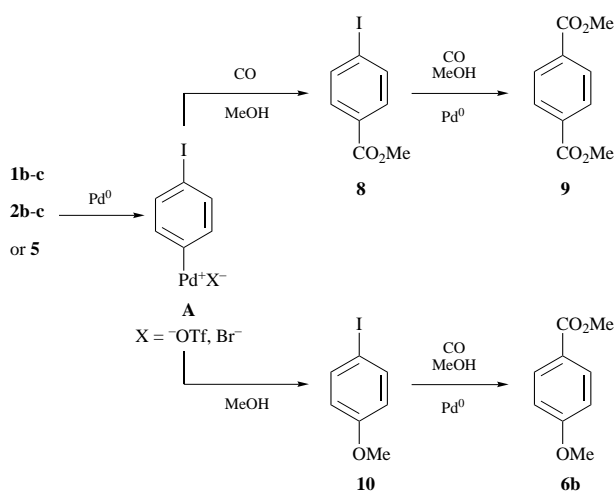
Entry	Iodonium salts	Reaction conditions ^a	Time (min)	Product	Isolated yield (%) ^b
1	Ph ₂ I ⁺ BF ₄ ⁻ 1a	A	20	PhCO ₂ Me 6a	83
		B	20	PhCO ₂ Ph 7a	91
2	<i>p</i> -MeOC ₆ H ₄ I ⁺ BF ₄ ⁻ 2a	A	30	MeO-C ₆ H ₄ -CO ₂ Me 6b	88
		B	30	MeO-C ₆ H ₄ -CO ₂ Ph 7b	92
3	2-Thienyl(Ph)I ⁺ OTs 3a	A	30	2-Thienyl-CO ₂ Me 6c	89
		B	30	2-Thienyl-CO ₂ Ph 7c	91
4	Ph-CH=CH-I ⁺ BF ₄ ⁻ 4	A	20	Ph-CH=CH-CO ₂ Me 6d	93
		B	20	Ph-CH=CH-CO ₂ Ph 7d	89
5	Ph ₂ I ⁺ OTf 1b	A	30	I-C ₆ H ₄ -CO ₂ Me 8	62
				MeO ₂ C-C ₆ H ₄ -CO ₂ Me 9	25
6	Ph ₂ I ⁺ (OTf) ₂ 5	A	30	8	91
				9	72
7	<i>p</i> -MeOC ₆ H ₄ I ⁺ OTf 2b	A	30	8 +	13
				9	
8	<i>p</i> -MeC ₆ H ₄ I ⁺ OTf 2c	A	30	I-C ₆ H ₄ -OMe 10	29
				MeO ₂ C-C ₆ H ₄ -OMe 6b	52
9	PhI ⁺ Br ⁻ C ₆ H ₄ - <i>p</i> -NO ₂ 1c	A	60	8	76

^a All the reactions were run with iodonium salts (1 equiv.) in the presence of CO (1 atm). Reaction conditions A: Pd(OAc)₂ (0.2 mol%), MeOH (1.2 equiv.), CO, DMF, rt; B: Pd(OAc)₂ (0.2 mol%), PhOH (1.2 equiv.), NaOH (1 equiv.), CO, DMF, rt. ^b The yields are isolated yields.

reacted with CO (1 atm) in the presence of methanol and phenol to furnish α,β -unsaturated esters **6d** and **7d** in 93 and 89% yields, respectively (entry 4). Unexpectedly, when diphenyl-

iodonium triflate **1b**¹⁰ instead of diphenyliodonium tetrafluoroborate **1a** was used as the iodonium source, the only difference being the different counterion, *p*-iodobenzoic acid methyl ester **8**¹¹ was obtained (62%) together with dimethyl terephthalate **9**[†] (25%) as a minor product (entry 5). Utilizing Zefirov's reagent **5**¹² as hypervalent iodine compound, treatment of **5** with CO in the presence of Pd(OAc)₂ (0.2 mol%) and methanol afforded methyl *p*-iodobenzoate **8** in 91% yield (entry 6). For the *p*-methoxyphenyl(phenyl)iodonium triflate **2b**,¹⁰ methyl *p*-iodobenzoate **8** (72%) was obtained as a major product along with dimethyl terephthalate **9** (13%) (entry 7). In the case of *p*-tolyl(phenyl)iodonium triflate **2c**,¹⁰ unexpected *p*-iodoanisole **10**[‡] was isolated as a minor product and methyl *p*-methoxybenzoate **6b** was obtained as a major product (entry 8). As indirect evidence of the incorporation of a methoxy group (entry 8), when the same reaction was conducted in PhOH, *p*-iodophenoxybenzene and the *p*-phenoxy ester were produced.

For the formation of the unusual methyl *p*-iodobenzoate with iodonium triflate, it is presumed¹³ that the intermediate *p*-iodophenylpalladium complexes **A** generated by oxidative addition of Pd⁰ species to the *para*-position of the phenyl group would be subjected to methoxycarbonylation to give **8**, which was subjected to further carbonylation to provide **9**. With reagent **2c**, the intermediate **A** generated would couple with MeOH without incorporation of carbon monoxide to afford *p*-iodoanisole **10** as an unexpected product along with ester **6b** after carbonylation (Scheme 1). As indirect evidence of the



Scheme 1

intermediacy of **8** and **10**, when readily available methyl *p*-iodobenzoate **8** and *p*-iodoanisole **10** were treated with CO and MeOH under the same conditions, the esters **9** and **6b** were also produced, respectively.

Finally, it is noteworthy that the reaction of iodonium bromide **1c**¹⁴ with carbon monoxide in methanol with Pd(OAc)₂ (0.2 mol%) as a catalyst under one atmosphere pressure of carbon monoxide at room temperature afforded methyl *p*-iodobenzoate **8** as the sole product in 76% yield (entry 9).

† **9**: TLC; SiO₂, EtOAc–hexane 1:10, *R*_f = 0.29; δ_H(400 MHz, CDCl₃) 3.95 (s, 6 H), 8.11 (s, 4 H); ν_{max}(KBr)/cm⁻¹ 3057, 2986, 1733, 1266; *m/z* 194, 193, 162 (base peak), 134, 102.

‡ **10**: TLC; SiO₂, EtOAc–hexane 1:10, *R*_f = 0.53; δ_H(400 MHz, CDCl₃) 3.78 (s, 3 H), 6.68 (m, 2 H), 7.55 (m, 2 H); ν_{max}(KBr)/cm⁻¹ 2985, 1374, 1242; *m/z* 234, 233 (base peak), 218, 91, 62.

In summary, Pd(OAc)₂ (0.2 mol%)-catalyzed carbonylation in the presence of methanol afforded aromatic methyl esters with diaryliodonium tetrafluoroborates or tosylates and *p*-iodophenyl-substituted esters with diaryliodonium triflates and bromides depending on the counterions of the iodonium salts.

Experimental

Preparation of methyl *p*-benzoate **8**

To a stirred solution of Zefirov's reagent [Ph(OTf)OI(OTf)Ph] (800 mg, 1.67 mmol) in MeOH (10 ml) under one atmosphere pressure of carbon monoxide at room temperature was added Pd(OAc)₂ (0.75 mg, 0.2 mol%). The reaction mixture was stirred at room temperature for 30 min and then extracted with diethyl ether (30 ml × 3). The organic layer was dried over anhydrous MgSO₄, and the solvent evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography (eluting with EtOAc–hexanes 1:10, *R*_f = 0.50) to afford **8** (264 mg, 91%); δ_H(400 MHz, CDCl₃) 3.91 (s, 3 H), 7.74 (m, 2 H), 7.80 (m, 2 H); ν_{max}(KBr)/cm⁻¹ 3057, 2987, 1726, 1269; *m/z* 262, 230, 127, 75 (base peak), 73.

Acknowledgements

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